Micro-liquid Chromatography-Electrospray/Ion Trap Mass Spectrometry for Detection of - Dibutyltin - in Natural Waters

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Introduction

Pharmaceutical Sources of Dibutyltin (DBT)

- Feed additive for chickens and turkeys - used as an antihilmentic.

Other Possible Environmental Sources of Dibutyltin

- Widely used as a plastic stabilizer in PVC products: PVC pipe (i.e., 1 lb of DBT for every 100 lbs of PVC), packaging materials, baking parchments.
- Breakdown product of Tributyltin.

Adverse Health Effects

DBT

- Significant neurotoxicity exhibited in immature brain cell cultures at 30 ppb.[1]
- 100% Suppression of natural killer lymphocytes function at approx. 3 ppm - 30% suppression at 150 ppb.[2]
- Potent teratogen if exposure is during period of organogenesis.[3]

Experimental[4]

Water Extractions

- water samples (1-2 L) are pH adjusted to approximately pH 2.5 with HCl (12N)
- The pH-adjusted waters are poured through prepped 48-mm nu*phase SPE C18 discs [using the Accuprep 7000™ manifold (CPI International)]
- Dried discs are then extracted with four 10-mL volumes of 99% methanol/1% acetic acid
- The extracts are then evaporated to 0.5 mL using nitrogen in a water bath 30 °C (TurboVap® II) (Zymark Corporation, Hopkinton, MA, USA).

Experimental - cont.

Analysis

- chromatography - micro-LC columns packed in-house: 160-∶m i.d. x 30-cm fused-silica columns (Polymicro Technologies, Phoenix, AZ). Packed with 10 to 12 cm of 5-∶m ODS-Hypersil (Shandon, Astmoor, England)
- mobile phase: isocratic mobile phase:

  80% methanol : 14% water : 6% acetic acid :

  0.1% tropolone (v/v/v/m)
- flow rates: 4 to 6 ∶L/min

Experimental - cont.

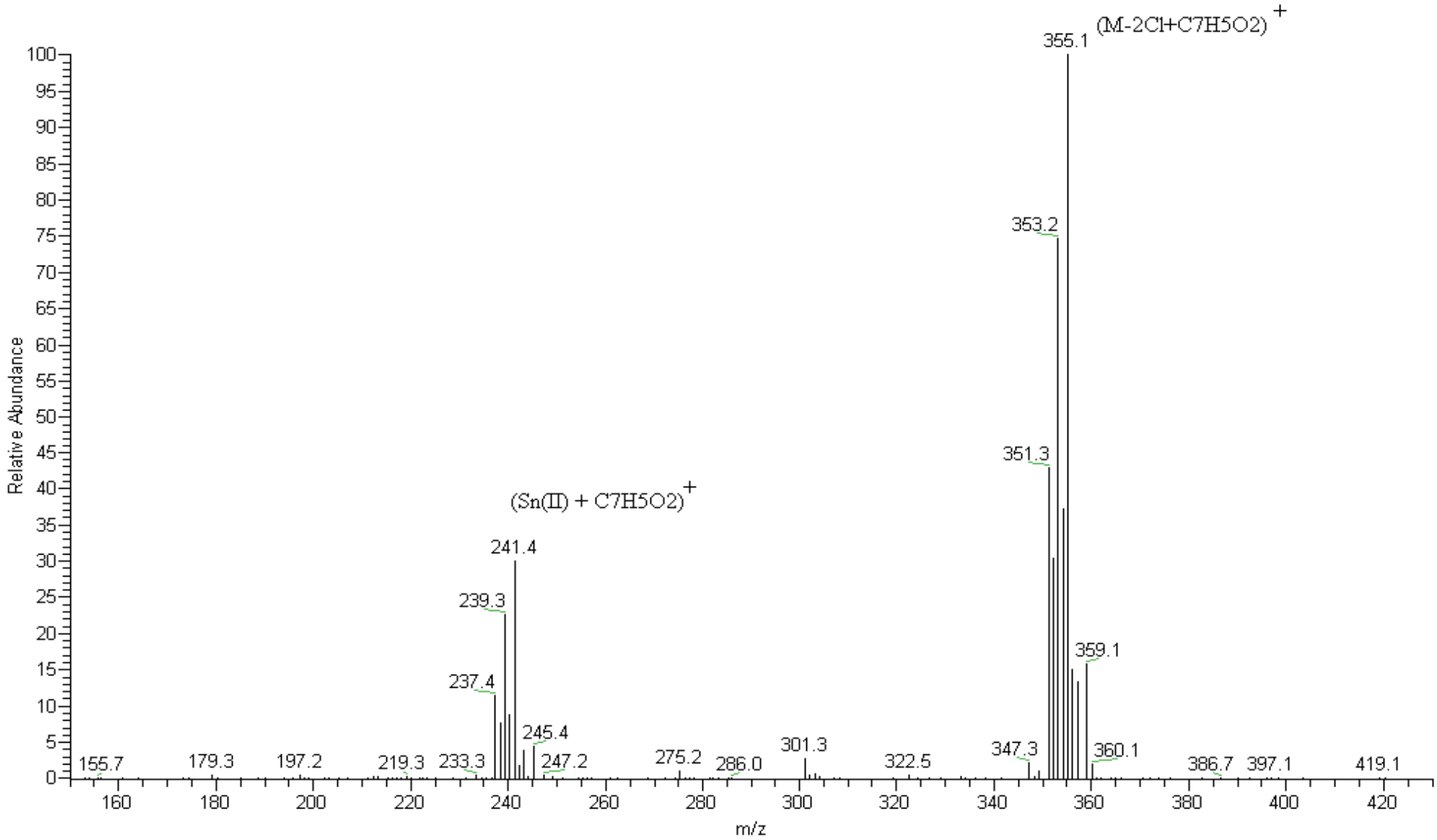
Analysis - cont.

- Mass Spectrometry - Finnigan LCQ™ , configured with an electrospray (ES) ion source
- positive ion mode
- ES needle: 4.5 kV to 5.2 kV
- 150 to 430 amu (full-scan mode) in

  3 microscans with an ion injection of 200 ms.

Results and Discussion

Spectrum of Dibutyltin



Results & Discussion

Amount of DBT found in Natural Waters

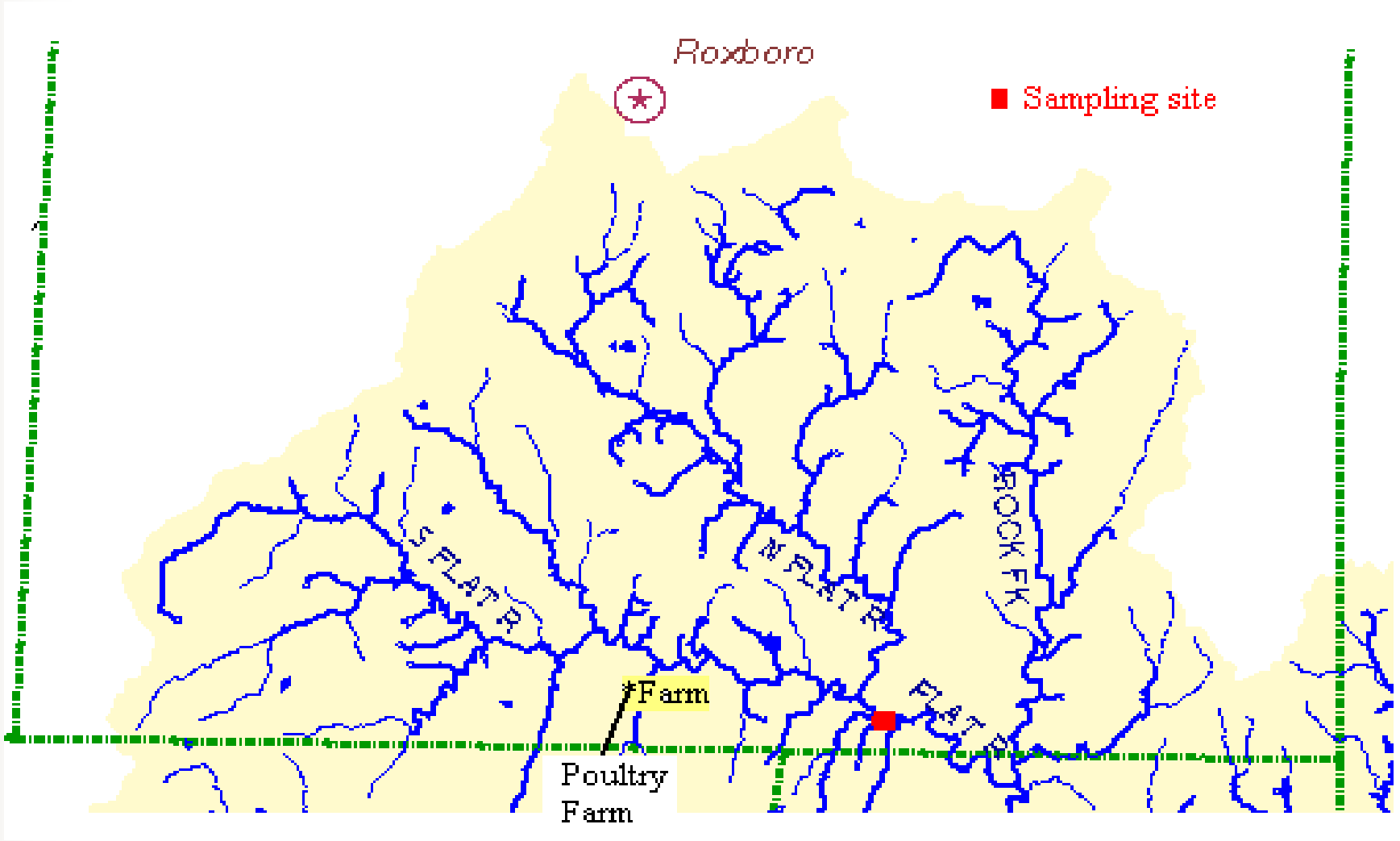
State	DBT avg. : g/L
North Dakota	ND[a]
Texas	ND
Maine	ND
Alaska	ND
North Carolina Site #1	1.3
North Carolina Site #2	2.0
North Carolina Site #3	2.6

[a]ND = not detected, below LOD (LOD = 970 pg – on-column)

Map of North Carolina Sampling Site #1

Sampling site

Map of North Carolina Sampling Site #2



Map of North Carolina Sampling Site #3

Conclusions

- LC/MS provides a low solvent usage (green), fast, and definitive method for determining dibutyltin in natural waters.
- Trace levels (ppb) of dibutyltin are present in some natural waters from various regions in the United States.

References

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2. Whalen, M.M.; Loganathan, B.G.; Kannan, K. "Immunotoxicity of Environmentally Relevant Concentrations of Butyltins on Human Natural Killer Cells *in Vitro*," Environ. Res. Section A **81** (**1999**) 108-116.

3. Ema, M.; Kurosaka, R.; Amano, H.; Ogawa, Y. "Comparative Developmental Toxicity of Di-, Tri- and Tetrabutyltin Compounds after Administration during Late Organogenesis in Rats," J. Appl. Toxicol. **16** (*1*) (**1996**) 71-76.

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